Effect of temperature and solvent composition on the unperturbed dimensions of polystyrene

A. Bazuaye and M. B. Huglin
Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK
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Several procedures have been used to establish and verify the unperturbed state of polystyrene in 1-chlorodecane ($\theta = 6.2^\circ$C) and 3-methyl cyclohexanol ($\theta = 98.4^\circ$C) as well as in other single solvents having $6.2^\circ < \theta < 98.4^\circ$. At each θ-temperature for a single solvent, the unperturbed state for a binary solvent was established in mixtures of 1-chlorodecane and 3-methyl cyclohexanol of varying composition. Viscometric measurements showed that neither the nature of the solvent nor the temperature affects the unperturbed chain dimensions appreciably. On the other hand, the unperturbed mean square radius of gyration measured directly by light scattering exhibits a definite decrease with increase in temperature, which accords qualitatively with the conformational energy calculations of Flory and co-workers.

INTRODUCTION

The unperturbed dimensions of a polymer coil can be realised in the solid state and examined by neutron scattering. Alternatively, viscometry and light scattering on solutions may be used, in which the θ-state corresponds to both upper and lower critical solution temperatures. Because it is more easily accessible, we shall be concerned here experimentally only with the former. When a single solvent is not available to yield a convenient θ-temperature, recourse is frequently made to binary solvent mixtures the variable composition of which affords, in principle, a range of different θ-temperatures. However, there are often practical restrictions imposed on the flexibility of such systems. These include (i) freezing of solvent(s), (ii) proximity of the θ-temperature to the boiling point(s) of solvent(s), and (iii) complete insolubility of polymer at all convenient working temperatures, when the proportion of bad solvent in the binary mixture exceeds a certain value. These points apply, for example, to polystyrene in benzene/methanol[1,2] or in ethyl acetate/ethanol[3].

At a fixed temperature, of course, there are numerous pairs of liquids[4] capable of yielding θ-compositions. Whether the unperturbed dimensions at a given temperature are single valued or are influenced by specific solvent effects within the mixed solvent has been the purpose of many investigations, but there is still not unanimity on this matter. Moreover, the temperature coefficient of the unperturbed dimensions does not always accord in size and magnitude with that determined by thermoelastic measurements on lightly cross-linked samples. The use of homologously related solvents to obtain different θ-temperatures and hence a temperature coefficient of unperturbed dimensions with minimal specific solvent effects has been reported[5].

To resolve some of the uncertainties indicated previously we report here studies on solutions of polystyrene (PS, subscript 2) in binary mixtures of 1-chlorodecane (CD, subscript 3) and 3-methyl cyclohexanol (MC, subscript 1). These solvent components are characterized by complete miscibility, low freezing-points and high boiling-points. Their θ-temperatures have been reported as *ca.* 6° [6] and *ca.* 98°C [7] respectively. Thus, binary mixtures encompassing the entire composition range of $\phi_1 = 0$ to $\phi_1 = 1$ (where ϕ denotes volume fraction) are capable of yielding values of $98^\circ > \theta > 6^\circ$C and hence a temperature coefficient of unperturbed dimensions over a rather wide span of temperature. The particular θ-temperatures have been pre-selected so as to coincide with those already known for single solvents. Hence, at any given θ, a direct comparison may be made between the dimensions in pure and mixed solvents. In no instance has absolute reliance been placed on literature values of θ in single solvents, since much uncertainty is evident on this score.

Previous studies on PS in *cis*-decalin/*trans*-decalin[8] and in cyclohexane/methyl cyclohexane[9] encompass rather short spans of temperature and, moreover, do not allow direct comparison with specific θ-conditions in single solvents.

EXPERIMENTAL

Materials.

Four nominally monodisperse polystyrene standards were obtained from Waters Associates Ltd. The quoted molecular weights were 1.1×10^5, 2.0×10^5, 4.8×10^5 and 2.7×10^6 and the samples are designated here as PS A, PS B, PS C, and PS D, respectively. For work in which polydispersity was not relevant, a sample PS 3 ($\bar{M}_w = 3.4 \times 10^5$) was used; this was kindly donated by Polymer Supply and Characterisation Centre, R.A.P.R.A., Shawbury, Shrewsbury, U. K. (courtesy of Mr. L. J. Maisey). The fact that the four standards actually possess a not inconsiderable polydispersity was later made

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known to us from the g.p.c. analyses at R.A.P.R.A. (courtesy of Mr. J. McConville). The peak maxima concurred well with the nominal molecular weights, but in increasing order of the latter the ratios $\bar{M}_w/\bar{M}_n$ were 1.15, 1.19, 1.35 and 1.94. (With particular regard to standard sample PS D it is interesting to note that Wolf *et al.*[10] observed differences between nominal and their own experimental data for both the molecular weight and the ratio $\bar{M}_w/\bar{M}_n$, the latter being actually *ca.* 2.0 instead of *ca.* 1.2. Their sample of nominal $\bar{M}_w = 2.5 \times 10^6$ was supplied by Pressure Chemical Co. It is not widely appreciated that the standards supplied by Waters Associates and by Pressure Chemicals originate from an identical source). The solvents CD, MC, diethyl oxalate, cyclohexane and cyclohexanol were dried rigorously and distilled at either atmospheric pressure or under reduced pressure. Purity was checked by boiling-point and refractive index. *Trans*-decalin was isolated from the commercial mixture of *cis* and *trans* isomers. Since others adopting this separation have not provided experimental datails, the method used by ourselves is summarized here: The *cis-trans* mixture (1 kg) was stirred with anhydrous $AlCl_3$ (10 gm) whilst heated under reflux until the development of a dark brown coloration (*ca.* 6h). After the mixture was cooled, it was rendered neutral by removing the HCl formed with several aqueous washings. Water was separated and the remainder dried with anhydrous $MgSO_4$ defore distillation at atmospheric pressure. The liquid distilling at 185°–190° was retained. This process was repeated on two more separate occasions starting with the commercial mixture. The combined distillates were fractionally distilled and the portion of b.p. 189–190°C collected. The yield was 15% based on the total initial mixture used. The density was 0.865 g/ml at 25°C and $\tilde{n}^D_{25} = 1.469$. The corresponding literature values are respectively 0.866 g/ml and 1.467 for the pure *trans* isomer and 0.892 g/ml and 1.479 for the pure *cis* isomer.

It should be mentioned that MC is regarded here as a single solvent, although this substance can exist as *cis* and *trans* isomers. The commercial product is mainly *cis* in nature and the composition is almost certainly unchanged on distillation since both isomers have the same boiling point.

Density

The densities of CD/MC mixtures at different temperatures were measured in stoppered Sprengl pyknometers. For other solvents, the densities and their temperature coefficients were taken from the literature. The density of amorphous PS at different temperatures was taken from the data of Beaman and Gramer[11].

Refractometry and light scattering (all at $\lambda_0 = 436$ nm):

Refractive indices $\tilde{n}_0$ of single solvents as well as those of eleven CD/MC mixtures were measured at different temperatures with a Pulfrich refractometer. Specific refractive index increments $d\tilde{n}/dc$ of solutions of PS 3 in pure and mixed solvents were determined at the θ-temperatures in a Brice–Phoenix differential refractometer calibrated with aq. KCl. Light scattering employing unpolarised incident light was conducted on a Sofica photometer calibrated with the makers' glass standard in conjunction with the Rayleigh ratio of benzene[12] at different temperatures. Solvents and solutions were clarified by passage through a pre-heated fine sinter, which was maintained at 10°C above the relevant θ-temperature.

Solution viscosity:

Viscosities were measured in an Ubbelohde suspended-level dilution viscometer and data were manipulated *via* simultaneous extrapolation of plots according to the Huggins and Kraemer equations. In mixed solvents, measurements were made at the θ-temperature. In single solvents, temperatures of θ, *ca.* $\theta + 1.5°$ and *ca.* $\theta + 3.0°$C were used.

Determination of θ-conditions:

The Flory–Shultz treatment[13], as described previously[14], was applied to the four PS samples in CD, MC and cyclohexane. Two rapid turbidimetric procedures (denoted here as C.B.1 and C.B.2) have been proposed by Cornet and Ballegooijen[15]. Of these, method C.B.1 for solutions of PS 3 in CD, MC and cyclohexane yielded the same θ-temperature as that obtained *via* the more laborious Flory–Shultz technique. Consequently, method C.B.1 was adopted for the remaining single solvents and for all the mixed solvents. Method C.B.2 was employed to establish the θ-composition for PS 3 in mixed solvents, the constant temperature maintained being the θ-temperature already established *via* C.B.1. A confirmation of θ-conditions was thus afforded. Polymer solutions covering a concentration range of *ca.* $\phi_2 = 1 \times 10^{-2}$ to 6×10^{-4} were stirred rapidly by a magnetic follower in a stoppered tube which fitted closely in the annulus of a double walled glass cell through which liquid at any desired temperature was circulated continuously. The first onset of turbidity was observed visually as the point at which the fine rulings on a graph paper were no longer discernible. The volume fraction ϕ_2 of PS in solution was calculated at each temperature from the density of solvent and that of amorphous PS. The volume fraction of MC in the mixed solvent is denoted by ϕ_1. The difference between this and the volume fraction in solution is extremely slight for dilute solutions.

PROCEDURE

The overall *modus operandi* is summarized by the following items (a)–(c) for a single solvent and by items (d)–(g) for a mixed solvent.

(a) Establish θ-temperature via C.B.1.
(b) Confirm by light scattering at this temperature.
(c) Confirm viscometrically from Mark–Houwink and Stockmayer–Fixman plots[16] at this temperature and also at temperatures close to it.
(d) At θ-temperature thereby established, determine θ-composition for CD/MC mixture *via* C.B.2.
(e) Confirm by obtaining same θ-temperature *via* C.B.1 for solutions obtained in the mixture yielded by (d).
(f) Verify by light scattering under these θ-conditions.
(g) Verify viscometrically from Mark–Houwink and Stockmayer–Fixman plots under θ-conditions.

RESULTS

Properties of solvents and solutions:

For CD/MC mixtures, the dependence of density ρ_0 on composition ϕ_1 is not linear, but for any particular composition the density varies linearly with temperature. Similar considerations apply to the refractive indices $\tilde{n}_0$ of mixed solvents. An attempt to derive the partial molar volume $\bar{V}_1$ of MC for different values of ϕ_1 from density data showed that this quantity was, to within the accuracy of the data, equal to the molar volume V_1. The experimental curve of $\tilde{n}_0$ *versus* composition lay in close agreement with the curve based on a mixing rule. This was determined from experimental refractive indices $\tilde{n}_1$ and $\tilde{n}_3$ in conjunction with measured densities. The agreement may well result from the close similarity of $\tilde{n}_1$ and $\tilde{n}_2$. Indeed, attempts, by means of light scattering[17], to determine the excess free energy of mixing the solvent components were vitiated for this very reason and the data obtained are not reported here. Physicochemical data appertaining only to the θ-temperatures are given in *Table 1*.

θ-*Conditions:*

Results embodying the different procedures are given in *Table 2*. By way of illustration, plots relating to only one set of conditions (for θ = 59.6°C) are shown in *Figures 1* and *2*. Flory–Shultz plots using phase separation data are not reproduced here, but the derived values of θ (°C) and the entropy of dilution parameter ψ_1 are respectively 6.2 and 0.47 for CD and 98.4 and 0.86 for MC.

Table 1 Characteristics of solvents and solutions at the θ-temperature

Solvent	Temp (°C)	$\tilde{n}_0$	ρ_0 (g/ml)	$d\tilde{n}/dc$ (ml/g)	δ_0[a] (cal/ml)$^{1/2}$
CD	6.2	1.452	0.884	0.165	8.1
trans-decalin	22.8	1.479	0.869	0.141	8.8
CD/MC (ϕ_1 = 0.218)	22.8	1.435	0.845	0.165	8.7
cyclohexane	35.0	1.427	0.766	0.184	8.2
CD/MC (ϕ_1 = 0.250)	35.0	1.446	0.869	0.168	8.8
diethyl oxalate	59.6	1.403	1.033	0.195	8.6
CD/MC (ϕ_1 = 0.505)	59.6	1.443	0.853	0.166	9.3
cyclohexanol	87.8	1.448	0.875	0.141	11.4
CD/MC (ϕ_1 = 0.900)	87.8	1.445	0.856	0.155	10.5
MC	98.4	1.446	0.853	0.154	10.8

[a] Solubility parameters of solvents at 25°C, taken from the literature[18] for four single solvents. Values for CD and MC estimated by comparison with structurally and chemically related compounds; for mixtures, δ_0 calculated therefrom using $\delta_0 = \phi_1\delta_1 + \phi_3\delta_3$

The slopes of Stockmayer–Fixman plots at temperatures slightly above the derived θ-temperature extrapolate to a value of zero at this temperature, which lends support to the validity of the θ-temperature. The interaction parameters χ_1 derived from the slopes were so close to 0.500 in magnitude (of the order of 0.499) that no attempt was made to isolate the enthalpic portion χ_H from their variation with temperature[19]; this is a consequence of the very short temperature range covered. Similarly in single solvents, the Mark–Houwink viscosity exponents υ at temperatures slightly above the derived θ-temperature extrapolate to a value of 0.50 at the latter temperature. This linear variation of υ with T has been used by Lath and Bohdanecký[5] to locate the θ-temperature. However, there is no firm theoretical basis for the linear form and it is essential that the temperature used be close to the θ-temperature.

Unperturbed dimensions:

The unperturbed dimensions expressed as $[\langle r^2\rangle_0/M]^{1/2}$, where $\langle r^2\rangle_0$ is the unperturbed mean square end-to-end distance, may be calculated from the viscosity constant K_θ *via* equation (1)

$$K_\theta = \Phi[\langle r^2\rangle_0/M]^{3/2} \tag{1}$$

Even before appropriate heterogeneity corrections are made the uncorrected value of Φ still seems a matter of some individual preference. Hence only the values of K_θ are listed in *Table 2*.

Light scattering on sample PS 3 yielded A_2 = 0 (where A_2 is the second virial coefficient) under all the θ-conditions (see *Table 3*). Although a molecular weight of 3.5 × 10^5 is normally large enough to allow the mean square radius of gy-

Table 2 θ-Conditions and related data for PS in pure and mixed solvents

		Mark–Houwink		Stockmayer–Fixman		θ-Temp (°C) determined via			
Solvent	Temp (°C)	$K \times 10^4$ (dl/g)	υ	$K \times 10^4$ (dl.g$^{-3/2}$mol$^{1/2}$)	Slope × 10^8 (dl.g^{-2} mol)	C.B.1.	C.B.2.	Stockmayer–Fixman[a]	Flory–Shultz
CD	6.2	6.61	0.50	6.90	0	6.0	–	6.2	6.2
CD	8.0	4.90	0.53	7.0	2.81	–	–	–	–
CD	9.5	4.47	0.54	7.0	5.19	–	–	–	–
trans-decalin	22.8	6.76	0.50	6.73	0	22.8	–	23.0	–
CD/MC (ϕ_1 = 0.218)	22.8	7.50	0.50	7.50	0	22.8	22.9	–	–
trans-decalin	24.5	5.37	0.52	6.75	3.20	–	–	–	–
trans-decalin	26.0	4.27	0.54	6.75	6.50	–	–	–	–
cyclohexane	35.0	8.15	0.50	8.40	0	–	–	35.1	35.1
CD/MC (ϕ_1 = 0.250)	35.0	7.58	0.50	7.40	0	35.0	35.0	–	–
cyclohexane	38.0	6.46	0.53	8.50	8.12	–	–	–	–
cyclohexane	40.0	4.90	0.55	8.50	12.5	–	–	–	–
diethyl oxalate	59.6	7.24	0.50	7.20	0	59.6	–	59.6	–
CD/MC (ϕ_1 = 0.505)	59.6	7.18	0.50	7.20	0	59.6	59.6	–	–
diethyl oxalate	62.0	6.31	0.515	7.20	3.06	–	–	–	–
diethyl oxalate	63.4	5.56	0.525	7.25	5.00	–	–	–	–
cyclohexanol	87.8	7.24	0.50	7.10	0	87.8	–	87.7	–
CD/MC (ϕ_1 = 0.900)	87.8	7.08	0.50	7.05	0	87.8	87.8	–	–
cyclohexanol	89.5	5.89	0.52	7.10	6.02	–	–	–	–
cyclohexanol	91.5	4.68	0.54	7.10	12.9	–	–	–	–
MC	98.4	6.76	0.50	6.50	0	98.0	–	98.4	98.4
MC	100.0	4.57	0.535	6.50	4.37	–	–	–	–
MC	101.5	4.36	0.54	6.60	8.75	–	–	–	–

[a] Temperature at which Stockmayer–Fixman slope equals zero taking all three temperatures into consideration for single solvents

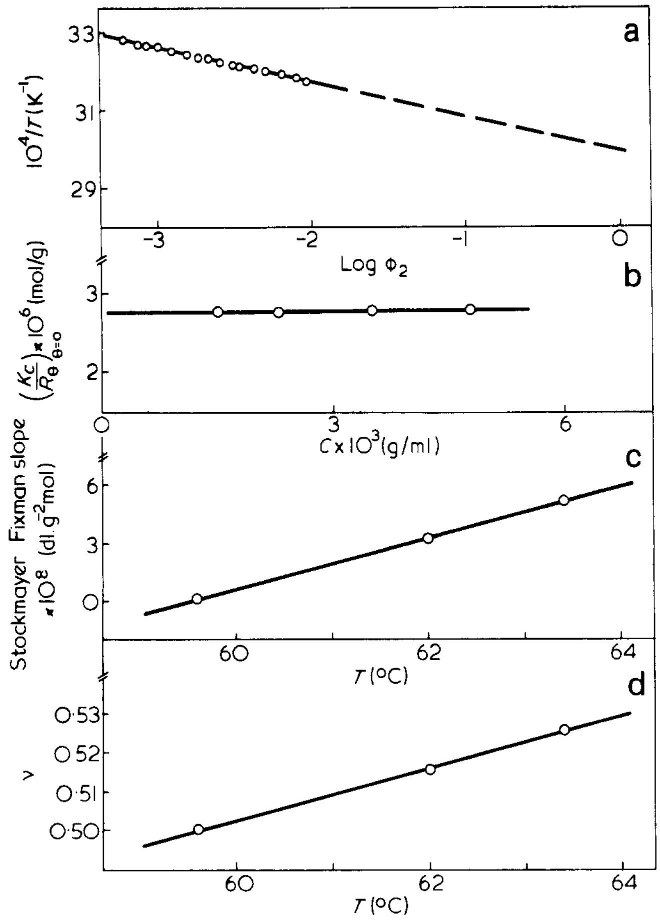

Figure 1 Theta conditions of PS in diethyl oxalate (a) Method CB1 to establish θ = 59.6°C (b) Light scattering plot at 59.6°C showing A_2 = 0 (c) Slopes of Stockmayer–Fixman plots as a function of temperature in the vicinity of θ (d) Mark–Houwink exponent as a function of temperature in the vicinity of θ

ration $\langle s^2 \rangle$ to be determined by light scattering, the paucity of the solvent medium reduced the dimensions to an extent such that the dimensions could not be obtained accurately for this sample.

Values of $\langle s^2 \rangle_{oz}$ for PS D, which was the sample of highest molecular weight, were readily measurable and are quoted in *Table 3*. Here again, A_2 = 0 and $\bar{M}_w$ is constant for all solvent media.

DISCUSSION

(a) θ-Temperatures

We compare first the θ-temperatures with the corresponding literature values. For CD, the temperature agrees exactly with that found by Orofino and Ciferri[6], who located it by extrapolation to zero of the A_2 values yielded by light scattering at different temperatures.

Although Reiss and Benoit[7] provided no information on the mode of obtaining the θ-temperature in MC, their quoted value of 98.0°C agrees well with the value found here. The θ-temperature in cyclohexane (to within 0.5°C) is now a matter of universal agreement.

Phase separation has yielded θ = 55.8°C in diethyl oxalate[9], but extrapolation of A_2 to zero is reported[20] to give a lower value of 51.5°C. It may be relevant that the latter lower θ-temperature was obtained with a PS sample of rather small molecular weight (1.7 x 10^5), which was also employed by similar means to yield θ = 83.5°C in cyclohexanol[20]. We have observed that sample PS D (M = 2.9 x 10^6) at a critical volume fraction is definitely not soluble in the relevant solvent at 51.5° or 83.5°C. Scornaux and Van Leemput[12], using a sample of M = 1.2 x 10^6, obtained θ = 89.2°C by extrapolation of A_2 to zero and θ = 85.1°C by extrapolating the slope of Stockmayer–Fixman plots to zero. The temperature reported here for cyclohexanol is intermediate between these two.

A standard compilation[21] lists θ-temperatures in *trans*-decalin ranging from 18.2° to 31°C. Additional reports include values of 19°–20°C (Lechner[22]), 20°C (Schulz and Lechner[23]), 20.4°C (Fukuda *et al.*[24]), 21°C (Roots and Nyström[25]), 21°–22°C (Berry[8]) and 25°C (Nyström *et al.*[26]). Fukada *et al.*[24] have noted a difference of *ca.* 3°C between the θ-temperatures of PS in trans-decalin, according to the nature of the solvent used in the anionic polymerisation of styrene. The light scattering data of Lechner[22], in particular afford strong corroboration of the validity of the θ-temperature used (19.6°C), but corresponding data presented here and relating to 22.8°C appear no less convincing. The presence of a small amount of residual *cis* isomer in the solvent used could, *a priori*, be advanced as a possible cause of the discrepancy. However, Berry[8] has demonstrated that this would lower, rather than raise, the θ-temperature relative to that in pure *trans*-decalin. It must be concluded,

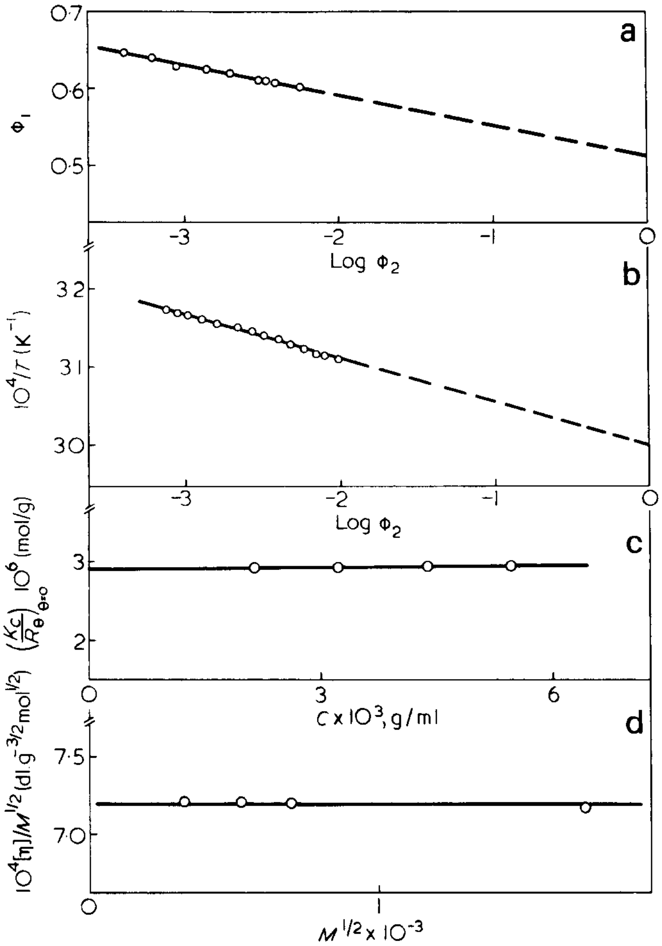

Figure 2 Theta conditons in CD/MC at 59.6°C (a) Establishment of critical binary solvent composition at a fixed temperature of 59.6°C by method CB2. (b) Confirmation of θ = 59.6°C by method CB1 using critical solvent mixture found in (a). (c) Light scattering plot in critical binary solvent at 59.6°C showing A_2 = 0
(d) Stockmayer–Fixman plot in critical binary solvent at 59.6°C showing slope = 0

Table 3 Light scattering results under θ conditions for samples PS3 and PSD

		PS 3			PS D		
Solvent	Temp (°C)	$\bar{M}_w \times 10^{-5}$	A_2	$\langle S^2 \rangle_z^{1/2}$	$\bar{M}_w \times 10^{-6}$	A_2	$\langle S^2 \rangle_z^{1/2} \times 10^8$ (cm)
CD	6.2	3.34	0	–	3.0	0	623 (±17)
trans decalin	22.8	3.44	0	–	3.0	0	601 (± 14)
CD/MC (ϕ_1 = 0,218)	22.8	3.35	0	–	2.8	0	555 (± 24)
cyclohexane	35.0	3.51	0	–	2.75	0	534 (± 24)
CD/MC (ϕ_1 = 0.250)	35.0	3.36	–	–	–	–	–
diethyl oxalate	59.6	3.59	0	–	3.1	0	526 (± 35)
CD/MC (ϕ_1 = 0.505)	59.6	3.44	0	–	2.9	0	493 (± 17)
cyclohexanol	87.8	3.56	0	–	2.9	0	486 (± 12)
CD/MC (ϕ_1 = 0.900)	87.8	3.60	0	–	2.8	0	444 (± 16)
MC	98.4	3.47	0		2.85	0	482 (± 15)

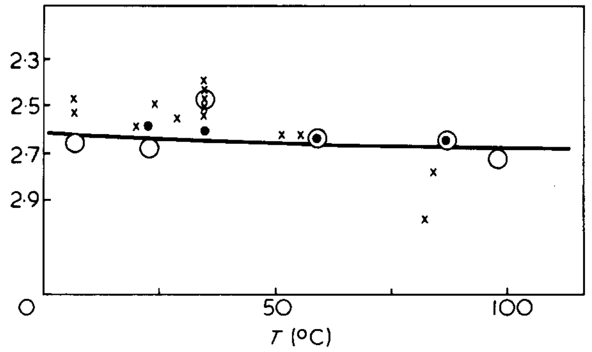

Figure 3 Determination of temperature coefficient of unperturbed dimensions from viscometric K_θ values in pure and mixed solvents (the literature values indicated refer to the same pure solvents as used here). ○ single solvents; ● mixed solvents; x literature values for single solvents

therefore, that the θ-temperature is still not known unequivocally.

(b) Viscosity Constants K_θ

With regard to unperturbed dimensions expressed as K_θ (dl $g^{-3/2}$ $mol^{1/2}$), comparison with literature values is hampered somewhat by the disparity among reported values relating to identical solvents. Thus, for PS in cyclohexane, these range between 7.4 x 10^{-4} and 9.1 x 10^{-4} with an average of 8.2 x 10^{-4}, which is close to K_θ = 8.4 x 10^{-4} in *Table 2*. Although two separately reported[9,20] values of θ in diethyl oxalate are both below the temperature of 59.6°C found here, the values of K_θ are actually the same in all three instances. On the other hand, in cyclohexanol, at two different reported θ-temperatures each below that of 87.8°C obtained here, the values of K_θ are 5.1 x 10^{-4} [20] and 6.1 x 10^{-4} [12], c.f. the value of 7.1 x 10^{-4} in *Table 2*. There is no previously published value for K_θ in MC and, for CD, the value in *Table 2* is lower than the only other published figures of 7.8 x 10^{-4} [6] and 8.4 x 10^{-4} [27]. Similarly, for PS in *trans*-decalin, the present value is smaller than the literature ones of 7.5 x 10^{-4} [24], 7.8 x 10^{-4} [20] and 8.2 x 10^{-4} [28].

In the mixed solvents containing a high content of MC, the values of K_θ are the same as in single solvents at corresponding temperatures. However, in the two remaining mixed solvents the values of K_θ are respectively lower and higher than those in single solvents. Nonethelesss the ratio K_θ (mixed solvent)/K_θ (single solvent) does not lead to a difference of greater than 8% between the derived dimensions $\langle r^2 \rangle_0/M$ (see equation 1).

(c) d ln $\langle r^2 \rangle_0/dT$ from viscosity

Using data solely for mixed solvents, a plot of ln K_θ vs. T is perfectly linear. However, in view of the fact that the differences between K_θ values in pure and binary solvents at each temperature do not appear very significant, no cognizance of this linearity is made in *Figure 3*, where the best straight line has been drawn to take account of *all* the data reported here. The slope yields a value of –0.3 (±0.3) x 10^{-3} deg^{-1} for the temperature coefficient $d\ln\langle r^2 \rangle_0/dT$. Literature values of ln K_θ for the same single solvents are indicated in *Figure 3*, but are excluded from consideration of the line and the slope.

(d) Directly measured unperturbed dimensions

There have been relatively few direct measurements of the unperturbed dimensions (U.D.) of polystyrene. For comparison, the values of U.D. in this context are regarded as those of $10^{18}\langle s^2 \rangle_{ow}/\bar{M}_w$ (with the mean square radius of gyration and molecular weight expressed in cm² and g mol^{-1} respectively). In obtaining this ratio, correction for heterogeneity is effected, viz:

$$\langle s^2 \rangle_{ow} = F < s^2 \rangle_{oz} \tag{2}$$

where $F = (h + 1)/(h + 2)$ and $h = 1/[(\bar{M}_w/\bar{M}_n) - 1]$

No published data are available for solutions CD, MC or diethyl oxalate. In cyclohexanol the U.D. has been found to be 7.52[12]. In cyclohexane the θ-temperature of deuterated PS is 30°C[29], and neutron scattering gives U.D. = 7.72 in dilute solution[29] whilst in this solvent light scattering on PS yields values of 7.06[10] and 7.9[30]. These data are similar in magnitude to the range of 7.27–7.85 obtained by Berry[8], who did, however, note a larger value (10.6) for PS of very high molecular weight in cyclohexane. Larger values of 11.5[12] and 12.2[31] have also been quoted recently.

From light scattering in *trans*-decalin, Fukuda *et al.*[24] obtained U.D. = 7.42–8.80, corroborated elsewhere[23,32] by a value of 7.75. Neutron scattering on bulk PS[33] yields what is asserted to be a constant value of the U.D. (actually the mean of two quoted values of 6.53 and 7.97). Moreover, these unperturbed dimensions were found to be sensibly constant[33] over a temperature range of 40°–160°C, that is, $d\ln\langle r^2 \rangle_0/dT = 0$.

(e) dln$\langle r^2 \rangle_0/dT$ from directly measured unperturbed dimensions

The values of $\langle s^2 \rangle_{oz}^{1/2}$ in *Table 3* were obtained from plots

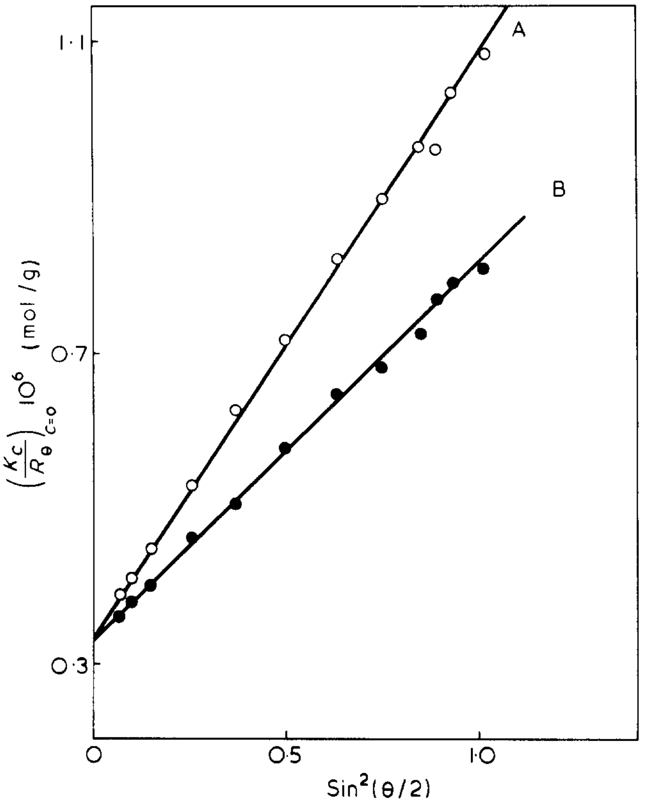

Figure 4 Reduced light scattering plots at infinite dilution for PSD in (A) CD at 6.2°C and (B) cyclohexanol at 87.8°C. Since the media are practically isorefractive under these conditions, the demonstrated difference in slopes results solely from the different unperturbed radii of gyration

of $(Kc/R_\theta)_{c=0}$ *versus* $\sin^2(\theta/2)$ (see, for example, *Figure 4*) and the quoted estimated errors are all *ca.* ± 2–3% except for the value obtained in diethyl oxalate where the error is *ca.* ± 7%. The polydispersity index, $\bar{M}_w/\bar{M}_n$, from g.p.c. analysis was 1.94 (a similarly high index for a Pressure Chemicals sample of comparable high molecular weight was observed by Wolf *et al.*[10]). Hence in equation (2) the factor F equals 0.673. Each experimental value of $\bar{M}_w$ (instead of the average value of 2.9×10^6 for PS-D) was used to compute the U.D., i.e. $10^{18} \times \langle s^2\rangle_{ow}/\bar{M}_w$, which ranged in magnitude from 4.74 to 8.71. The maximum relative error in ln (U.D.) was calculated from the errors in $\langle s^2\rangle_{ow}$ and $\bar{M}_w$ and is indicated by the length of the error bar for each point in *Figure 5*, which shows the variation of ln (U.D.) with temperature. The slope yields $d\ln\langle r^2\rangle_0/dT = -4.7\ (\pm 0.9) \times 10^{-3}$ deg^{-1} for data in single solvents and in binary solvents, although at corresponding temperature ln(U.D.) for the latter is slightly smaller than the value in the former.

Using iso-refractive components of a mixed solvent, Wolf *et al.*[10] obtained two θ-temperature (endothermal and exothermal) separated from each other by 22°C. The U.D. at each was identical (7.9) and was similar to the value in cyclohexane (7.2) as well as to the mean of several literature values in this solvent. On the other hand, Yamakawa *et al.*[34] have observed that the U.D. in a mixed solvent is significantly larger than in cyclohexane. Elias and Etter[35] were the first to note that variable unperturbed dimensions of PS are exhibited in two different solvent/precipitant mixtures both characterised by $A_2 = 0$. It is established that selective adsorption plays a role in these sytems. Cowie[4] has examined the influence of numerous binary solvents on the U.D. of PS at 35°C and found from viscosity data that K_θ varied considerably. From light scattering the effect was smaller, the ratio $\langle s^2\rangle_{oz}^{1/2}$ (mixed)/$\langle s^2\rangle_{oz}^{1/2}$ (single) ranging from 0.96 to 1.07. This variation among the radii of gyration seems significant insofar as it exceeds the limits of experimental uncertainty. Indeed other work[10] quotes this uncertainty to be ±1.5%, which is better than we have been able to claim.

Selective adsorption is not manifested experimentally in the present systems, but this does not imply that it is absent. It is merely a consequence of the close similarity of $\tilde{n}_1$ and $\tilde{n}_3$ with the result that $d\tilde{n}_0/d\phi_1$ is very small. To obtain a significant value of 0.1 ml/g for the selective adsorption parameter γ_1 in equation (3), the measured molecular weight M^* in a mixed solvent would be only *ca* 2.4% different from the true molecular weight M measured in a single solvent and this difference is well within the experimental error in any molecular weight determination by light scattering

$$M^*/M = [1 + \gamma_1(d\tilde{n}_0/d\phi_1)/(d\tilde{n}/dc)]^2 \qquad (3)$$

Irrespective of whether or not selective adsorption is manifested, there is ample published evidence that the unperturbed dimensions are influenced by strong differences in polarity among the constituents of the solution. One approximate criterion of this is the solubility parameter, as discussed by Cowie[4]. Another, as proposed by Benoit and Dondos[2] is the excess free energy of mixing, ΔG^E, of the liquids comprising the binary solvent. Non-ideality can be manifested by positive or negative values of ΔG^E. If the former, K_θ (mixed) should be greater than K_θ (single), whereas if ΔG^E is negative the opposite holds. The tendency for the unperturbed dimensions (U.D. or K_θ) in mixed solvents to be very slightly smaller than the corresponding ones in single solvents for the present systems suggests that the values of ΔG^E under the prevailing conditions of composition and temperature may be negative. However, as stated, this has not been subjected to experimental verification.

Consideration of the solubility parameters δ_0 of pure and mixed solvents (*Table 1*) does not yield any clear pointers to the role of sharp differences in polarity on unperturbed dimensions. Thus, literature values of δ_2 for PS range between the two values of δ_0 quoted for the solvents used at 59.6°C. On the other hand, (i) the values of δ_0 for *trans*-decalin and the more polar liquid diethyl oxalate are almost the same, (ii) the values of U.D. and K_θ in a single solvent are very similar at 87.8° to those in a binary mixture despite the reasonably large difference between the δ_0 values of the liquids in question. On the whole we are inclined not to attach much quantitative significance to the role of δ_0 vis à vis δ_2 in this context.

In *Figure 5* the values of U.D. in the region 20°–35° accord well with literature values. Despite the error limits, the

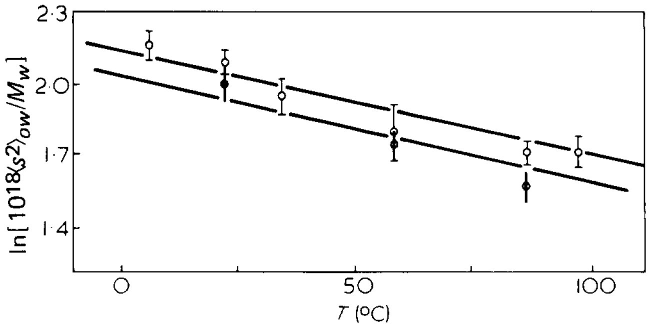

Figure 5 Determination of temperature coefficient of unperturbed dimensions from light scattering data in single ○ and mixed ● solvents

temperature coefficient of ln (U.D.) is certainly negative and of a magnitude greater than found hitherto by either light scattering or viscosity. The error in obtaining a radius of gyration by neutron scattering is greater (see *Figure 4* in reference 29) than by light scattering and it is perfectly feasible for the neutron scattering data of Ballard *et al.*[33] to accord with a negative temperature coefficient of the unperturbed dimensions (as found *via* the same technique by Benoit *et al.*[36]), although the magnitude of this coefficient would be smaller than found here.

Relevant references and further discussion on these as well as thermoelastic methods have been presented by Flory *et al.*[37], who used conformational energy analysis to calculate $d\ln\langle r^2\rangle_0/dT = -0.3 \times 10^{-3}$ to -1.5×10^{-3} deg^{-1}, depending on the choice of energy terms assumed. Further calculation failed to provide a positive temperature coefficient for any permissible combination of energies. This result together with the present findings does resolve, albeit qualitatively, the contentious issue of the algebraic sign of $d\ln\langle r^2\rangle_0/dT$ for polystyrene.

(f) Universal viscosity constant Φ

Finally, we report on the Flory constant Φ appearing in equation (1). It is readily shown that under θ-conditions this quantity is given by:

$$\Phi = [\eta]_\theta \bar{M}_w / 6^{3/2}(\langle s^2\rangle^{1/2}_{oz})^3 \qquad (4)$$

Ideally Φ should be calculated from the number average quantities $\bar{M}_n$ and $\langle s^2\rangle^{1/2}_{on}$. However, as indicated by Kurata and Stockmayer[38], if the respective weight average and z-average quantities (i.e. those measured directly by light scattering) are combined with $[\eta]_\theta$, then the derived Φ must be divided by a heterogeneity factor, q_z, in order to increase it to the correct Φ.

$$q_z = (h+1)\Gamma(h+1.5)/(h+2)^{3/2}\Gamma(h+1)$$

For sample PS D, use of the value $h = 1.064$ yields $q_z = 0.506$. Combination of experimental $[\eta]_\theta$ values with those of $\langle s^2\rangle^{1/2}_{oz}$ in *Table 3* yields values of Φ, which display some variation primarily because $\langle s^2\rangle^{1/2}_{oz}$ changes more rapidly with temperature than does $[\eta]_\theta$. The average value in conjunction with $q_z = 0.506$ gives a corrected average of $\Phi = 2.67 \times 10^{21}$ mol^{-1}.

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